A Mechanism for the Mullins Effect

*David E. Hanson, T-12; and Marilyn Hawley and Robert Houlton, MST-8*

Under repeated tensile strain, many particle-filled polymers such as silica-filled polydimethylsiloxane (PDMS), exhibit a reduction in stress after the initial extension, the so-called Mullins Effect [1] (see Fig. 1). Understanding the underlying physical mechanism is considered crucial to the development of predictive constitutive and aging models for filled polymers. However, despite more than 50 years of research, the origin of the Mullins Effect is still considered "one of the most important problems in rubber elasticity" [2]. We have developed a theoretical framework that suggests a mechanism to account for this effect [3]. Qualitatively, it accounts for most of the phenomenology associated with the Mullins Effect and makes an additional prediction: stress softening should not occur when the second strain axis is perpendicular to the initial strain axis. This has now been confirmed by experiments at the Laboratory.

Silica-filled PDMS is a material with widespread industrial uses as well as for cushions and mechanical supports in nuclear weapons. It derives its strength by virtue of the continuous, high functionality network that arises due to polymer chains adhering to the surfaces of silica filler particles by Van der Waals' and electrostatic forces. Chain entanglements, created during material preparation, can be permanently removed, under tensile strain, by chains sliding past one another at a connection point on a particle surface, by temporarily breaking (and then reforming) the weak Van der Waals' and electrostatic bonds. Previous estimates of this binding energy and the entanglement density are consistent with the strain energy observed in experiments. We propose that it is this removal of entanglements that produces the initial stress and that the stress observed during the second and subsequent strains can be attributed to elastic chain forces. For subsequent strains, larger than the first, new entanglements will be encountered and similarly removed, causing the stress to recover to the initial strain levels as shown in Fig. 1. This accounts for the material's apparent *memory* of its previous maximum strain state. Clearly, whether two proximate chains are entangled depends on their orientation with respect to the strain axis. It follows that, under tensile strain, only those entanglements associated with the strain axis are removed; entanglements associated with strains along axes perpendicular to the first strain would likely not be affected. From this observation, we can then predict that, if the material is subsequently strained along an axis orthogonal to the first strain axis, strain softening should not be observed. The experimental data shown in Fig. 2 confirms that this is indeed the case.

The shape of our stress vs strain curves for the initial extension (Fig. 1), which is typical of other experimental results in the literature, exhibits a steep increase in stress, followed by a more gradual, nearly linear increase with strain up to the point of tensile failure. According to

Fig. 1.
Sequential tensile strain cycles for virgin silica-filled PDMS sample showing stress softening: first pull to 100% (circles), second pull to 200% (triangles), third pull to 300% (diamonds). Also shown is the initial stress/strain for a separate sample pulled to 300% (squares).
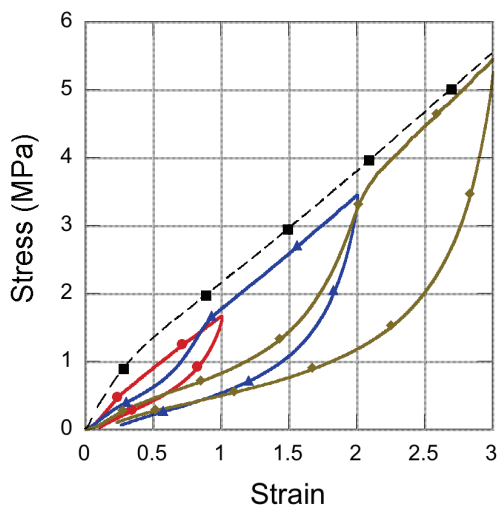
our proposed mechanism, the stress is due to the rate (with respect to strain) at which chain entanglements are removed. Neglecting for the moment the fact that the chains initially have slack, we conjecture that the chain-crossing rate is proportional to the angular density of chain end-to-end vectors, $s(\lambda) = \alpha H(\lambda)$, where s is the stress, λ is the extension factor, α is a proportionality constant, and H is the angular density of chain end-to-end vectors. By assuming the tensile strain is described by an affine transformation, we can obtain an expression for the average end-to-end angle as a function of λ and use its inverse as an estimate for the angular density:

$$H(\lambda) = \theta_{avg}^{-1} = \left[\frac{2}{\pi} \int_0^{\frac{\pi}{2}} cos^{-1} \left(\frac{\lambda \cos\theta}{\left[\frac{\sin^2\theta}{\lambda} + \lambda^2 \cos^2\theta \right]^{1/2}} \right) d\theta \right]^{-1}$$

As shown in Fig. 3, this function is in qualitative agreement with the experimental initial stress. We feel that our theoretical and experimental work provides a significant step in understanding stress softening in filled polymers.

For more information contact David Hanson at deh@lanl.gov.

[1] L. Mullins, *Rubber Chem. and Tech.* **42**, 339–361 (1969).
[2] M. Mark, et al., *Physical Properties of Polymers* (American Chemical Society: Washington, D.C., 1984).
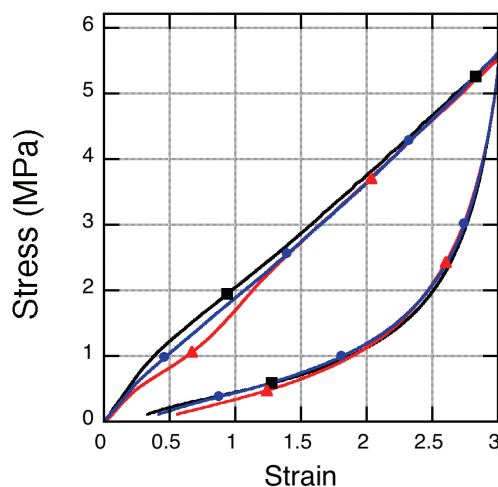[3] David E. Hanson, et al., *Polymer* **46**, 1089–10995 (2005).

Fig. 2.
Tensile stress/strain for secondary strain for small dog-bone samples cut and strained: perpendicular to initial strain axis (circles), and parallel (triangles). Also shown for comparison is initial stress/strain for a control sample (squares). Note that stress softening is not apparent in the secondary stress curve strained perpendicular to the original strain axis.
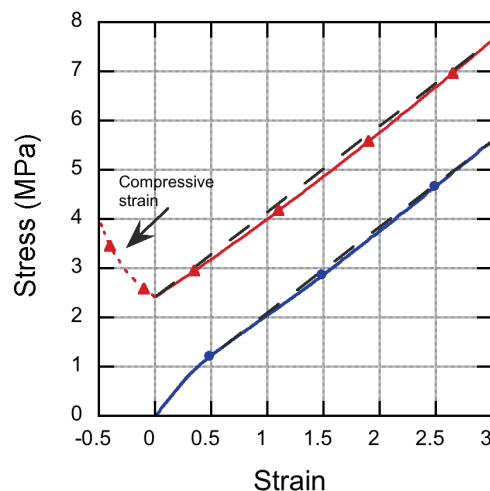

Fig. 3.
Comparison of angular density of chains function, H(λ) (triangles), and experimental data (circles). The experimental data is for the initial tensile strain and the angular density function has been scaled to have the same slope as the experimental data. Also shown adjacent to each curve is a straight line (dashed) for comparison. H(λ) for compressive strains ($\lambda< 0$) is also shown.